La(Sr)Ga(Fe)O_3 Perovskite Oxide as a New Mixed Conductor for an Oxygen Permeating Membrane

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Oxygen permeating property of Fe doped $LaGaO_3$ based perovskite oxide was investigated in this study. Fe doped $La_{1-X}Sr_XGaO_3$ exhibits high total conductivity (～4 S/cm) and high oxygen permeation rate. In particular, the highest total conductivity and oxygen permeating rate were attained at $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$. At this composition, oxygen permeation rate from air to He was as high as 2.5cc/min･cm^{-2} at 1273 K and 0.3 mm membrane thickness. Oxide ion conductivity was estimated with ion blocking method. The hole conduction was dominant in LSGF in air, however, high oxide ion conductivity of (～1 S/cm) was exhibited in LSGF at 1173 K.

Partial oxidation of CH_4 is attracting much attention, since the reaction gives a synthesis gas at $CO:H_2$=1:2 which is suitable for synthesis of methanol or hydrocarbons. Pure oxygen gas is an essential reactant for this reaction and as far as the cost is concerned, separation of air into O_2 and N_2 by a simple method should be considered. Separation of air into O_2 and N_2 by a mixed electronic and oxide ionic conducting ceramic membrane is an ideal method for obtaining pure oxygen because of its simple structure and low energy consumption.[1)] It is reported that $SrFeCo_{0.5}O_3$ is stable against reduction and it can be used for the oxygen permeating membrane for the partial oxidation of methane.[2,3)] However, further improvement in oxygen permeating rate is required for the application of the mixed electronic-oxide ionic conductor to the oxygen generator for CH_4 partial oxidation. In this study, mixed electronic and oxide ionic conductivity in Fe doped La(Sr)GaO_3 was investigated.

Preparation of Fe doped $LaGaO_3$ was performed by a conventional solid state reaction using La_2O_3 (99.99%), $SrCO_3$ (reagent grate), Ga_2O_3 (99.99%), and Fe_2O_3 (99.5%). Disks sintered at 1723 K were ground to 0.5mm in thickness with diamond wheel. Each disks were painted on both surfaces with $La_{0.6}Sr_{0.4}CoO_3$ (LSC) slurry at 10mm in diameter in order to improve the surface activity for oxygen dissociation. Permeating oxygen from air to He was analyzed by using a gas chromatograph. Pyrex glass ring was used for sealing gas. Electrical conductivity was measured with DC four-probe method in the gas flow cell.

Permeation rate of oxygen through Fe doped $LaGaO_3$ membrane (0.5 mm thickness) as a function of X value in $La_{1-X}Sr_XGa_{0.6}Fe_{0.4}O_3$. Oxygen permeation rate increased with increasing amount of doped Sr and it attained a maximum at X=0.3. At this composition, oxygen permeation rate of 1.8cc-STD/cm^2･min was achieved at 1273K. Therefore, the optimized X value for oxygen permeation in $La_{1-X}Sr_XGa_{0.6}Fe_{0.4}O_3$ exists at X=0.3. Since the highest electrical conductivity was also exhibited at X=0.3, increasing amount of Sr enhanced the amount of oxygen vacancy resulting in the improved oxide ion conductivity in $LaGaO_3$ based oxide. Consequently, the highest oxygen permeating rate was obtained at X=0.3. It was reported that oxygen permeation rate of $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_3$ was 2.1cc-STD/cm^2･min at 1127K under similar condition.[4)] Considering the oxygen permeating rate of 1.8cc-STD/cm^2･min at 1273K, it can be said that $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$ (LSGF) exhibits the high oxygen permeation rate and this LSGF is promising as an oxygen separating membrane from air.

Effects of the thickness of $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$ (denoted as LSGF) membrane on the oxygen permeation rate was further studied and the results are shown in Fig.1. In agreement with the theory, oxygen permeation rate monotonously increased with decreasing thickness of the membrane and the oxygen permeating rate at 1173K attained to a valve of 2.5cc-STD/cm^2･min when the thickness of the LSFC membrane was 0.3 mm. Therefore, rate determining step for oxygen permeation through LSGF membrane seems to be bulk diffusion process and consequently, it is expected further higher oxygen permeation rate is obtained by decreasing thickness of membrane. Oxide ion conductivity was estimated with ion blocking method. The hole conduction was dominant in LSGF in air, however, high oxide ion conductivity of (～1 S/cm) was exhibited in LSGF at 1173 K.

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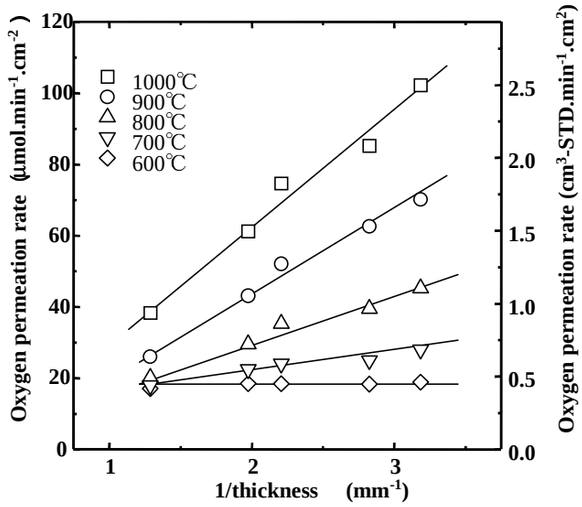

Fig. 1 oxygen permeating rate through $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$ as a function of thickness.